DETERMINATION OF RADIUM 226 IN URANIUM BEARING REFERENCE MATERIALS FOR CERTIFICATION PURPOSES

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FINAL REPORT

BY

BRITISH COLUMBIA RESEARCH COUNCIL

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada.

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SUMMARY

Radium 226 activity determinations were made for four independent subsamples of tne uranium bearing materials designated BL-5, BL-4a, DH-1a and DL-1a. Each subsample was digested to obtain radium in solution followed by precipitation with barium sulphate and activity counting using alpha spectroscopy. N.B.S. Standard Reference Material 4957-17 was used for calibration. Tne relative one-sigma level uncertainty in the net count response for all measured sample aliquots, and the one-sigma level uncertainty in tne derived calibration parameters, were within contract specifications. The measured Ra-226 activities were as follows:

Reference Material	Ra-226 Activity ($Bq.g^{-1}$)			
	Subsample 1	Subsample 2	Subsample 3	Subsample 4
BL-5	801	959	1007	1032
BL-4a	16.28	15.55	16.43	17.95
DH-1a	34.90	32.02	35.77	34.66
DL-1a	1.425	1.527	1.553	1.422

INTRODUCTION

B.C. Research has been contracted by the Department of Supplies and Services, Canada, to participate in a program to establish recommended values for the activity of the isotope radium-226 contained in each of four Canadian Certified Reference Materials Project (CCRMP) uranium and uranium-thorium ore materials. This report presents the results of the determination of radium-226 activity in four subsamples of each of the four reference materials, performed during the period September-December, 1982.

PROCEDURES

LABORATORY

All work was performed in the laboratories of the Division of Extractive Metallurgy, B.C. Research, 3650 Wesbrook Mall, Vancouver, B.C. V6S 2L2.

ANALYSTS

Tne analytical work was performed by G.P. Lee under the direction of B. Caugnlin.

REFERENCE MATERIALS

200 g samples of the uranium bearing reference materials designated BL-4, DH-1a and DL-1a, and 100 g of the reference material designated BL-5, were received at B.C. Research on 3 September, 1982.

Each sample was transferred to a large bottle and thoroughly mixed. Four subsamples, each weighing 1.000 g were weighed out from each mixed sample.

RADIUM-226 DETERMINATIONS

A detailed description of the analytical procedures used for radium-226 determination in each subsample of each reference material is given in Appendix 1.

CALIBRATION

Standard Reference Material 4957-17a Gamma Ray Standard for Radium-226 from the National Bureau of Standards, Washington, D.C. was used for calibration (Appendix 2). Tne ampoule as received from N.B.S. contained 0.500 µg ± 1.8% radium-226.

A standard solution containing 18.285 $Bq.mL^{-1}$ was prepared for calibrations for the analysis of samples BL-5, BL-4a and DH-1a. A 1.8285 $Bq.mL^{-1}$ standard was prepared for calibrations for the analysis of sample DL-1a.

Aliquots of the standard solutions were taken and treated in the same manner as samples, starting at step 3 of the analytical procedure (Appendix 1) to produce efficiency standards. This procedure minimized sample/calibration differences. The standards were counted in the same manner and with the same geometry as the reference material samples. Efficiency standards were counted in each detector used to determine calibration factors (counts. $bq^{-1}.s^{-1}$). The unknown samples were then counted. Examples of calculations to determine the one sigma uncertainties in calibration factors are shown in Appendix 3.

INSTRUMENTATION

The alpha spectroscopy system used for the counting of radium-226 activity comprised the following:

- 4 PGT E300-30-100 silicon surface barrier detectors
- 4 ND 404 preamplifiers
- 4 ND 500 amplifiers
- 4 Gamma Products VC5 Vacuum chambers
- 2 Mech Tronics ND 250 dual HV bias supply
- ND 569 gated analog router
- ND 60 multichannel analyzer.

The Ba-133 recovery tracer was counted on a gross gamma system comprising:

- Bicron NaI (Tl) detector 2M2/2
- ND 251 HV supply
- ND 512 amplifier and SCA
- ND 719 counter

RESULTS

Tables 1, 2, 3 and 4 give the radium-226 results for each reference material with the associated one sigma uncertainty components, and the subsample masses. The relative one sigma level uncertainty in the net count response for measured sample aliquots, and the one sigma level uncertainty in the derived calibration parameters were less than 0.41% for all subsamples of BL-5, BL-4a and DH-1a, and less than 1.1% for subsamples of DL-1a. Contract specifications with regard to these uncertainties were therefore met.

The components entering the counting precision calculation are:

(i) net count response
(ii) background counts
(iii) calibration factor error
(iv) factors due to tracer recovery

A sample calculation, shown in detail in Appendix 4, illustrates the relative magnitude of each factor. The results of this calculation for sample DH-1a, subsample 3 are typical for the analyses performed in this work, and show that the contribution of each factor to the one sigma uncertainty is:

net count response	17.41%
background	0.001%
calibration factor	55.14%
tracers	27.45%

TABLE 1

Radium-226 Analysis of Uranium Bearing
Reference Material BL5

Subsample #	1	2	3	4
Activity ($Bq.g^{-1}$)	801	959	1007	1032
σ Total (%)	0.45	0.46	0.44	0.43
σ net counts (%)	0.24	0.23	0.21	0.21
σ calibration (%)	0.31	0.33	0.31	0.31
σ tracers (%)	0.22	0.22	0.23	0.22
Subsample mass (g)	1.000	1.000	1.000	1.000

TABLE 2

Radium-226 Analysis of Uranium Bearing
Reference Material BL-4a

Subsample #	1	2	3	4
Activity ($Bq.g^{-1}$)	16.28	15.55	16.43	17.95
σ Total (%)	0.46	0.47	0.48	0.47
σ net counts (%)	0.25	0.26	0.26	0.26
σ calibration (%)	0.31	0.33	0.32	0.31
σ tracers (%)	0.23	0.22	0.24	0.23
Subsample mass (g)	1.000	1.000	1.000	1.000

TABLE 3

Radium-226 Analysis of Uranium Bearing
Reference Material DH-1a

Subsample #	1	2	3	4
Activity ($Bq.g^{-1}$)	34.90	32.02	35.77	34.66
σ Total (%)	0.43	0.45	0.45	0.45
σ net counts (%)	0.18	0.21	0.19	0.19
σ calibration (%)	0.31	0.31	0.33	0.32
σ tracers (%)	0.24	0.25	0.23	0.25
Subsample mass (g)	1.000	1.000	1.000	1.000

TABLE 4

Radium-226 Analysis of Uranium Bearing
Reference Material DL-1a

Subsample #	1	2	3	4
Activity ($Bq.g^{-1}$)	1.425	1.527	1.553	1.422
σ Total (%)	1.43	1.48	1.47	1.48
σ net counts (%)	0.86	0.80	0.79	0.83
σ calibration (%)	1.01	0.99	1.09	1.04
σ tracers (%)	0.72	0.73	0.73	0.70
Subsample mass (g)	1.000	1.000	1.000	1.000

R.W. Lawrence, Ph.D.
Senior Research Engineer
Division of Extractive Metallurgy

ON BEHALF OF B.C. RESEARCH

A. Bruynesteyn, Head
Division of Extractive Metallurgy

APPENDIX 1

ANALYTICAL PROCEDURE FOR RADIUM-226

ANALYTICAL PROCEDURE FOR RADIUM 226

1. Accurately weigh 1 g of each subsample of each reference material into a 250 mL beaker. Wet, add an appropriate aliquot of Ba-133 tracer, 10 mL concentrated HNO_3 and 5 mL $HClO_4$. Digest to dryness (3 times). Transfer to a platinum crucible with a minimum amount of water. Evaporate to dryness. Add 10 mL HF and digest to dryness (3 times).

2. Dissolve residue completely in 5 mL of HNO_3 and several mL of deionized water. Make up to volume in a 50 mL volumetric flask with deionized water.

3. Measure an aliquot in a clean unscratched beaker and bring to 50 mL with deionized water. Add 1 mL $BaCl_2$ solution (=0.3 mg Ba^{++}) and dropwise 2 mL 9M H_2SO_4 under stirring.

4. After 30 minutes filter the solution through a 0.45 µm membrane filter.

5. Transfer the filter and precipitate to the original beaker. Rinse filter tower with 5 mL DTPA solution. Collect the DTPA into the beaker containing the filter.

6. Warm the beaker gently at low heat; after 20 minutes the $BaSO_4$ will have dissolved.

7. Remove the membrane filter and rinse well. Keep the amount of water used in the rinsing to 15 mL.

8. Add 1 mL 20% $NaSO_4$ and enough 2.5 M $HClO_4$ to bring pH to 4.

9. Heat solution gently to expel radon.

10. After 10 minutes of heating, cool the solution and filter through a 0.45 μm membrane filter. Discard the filtrate.

11. Dry the filter containing $Ba(Ra)SO_4$ carefully and measure the radiochemical recovery of Ba-133 and the alpha activity of Ra-226.

Ref. D. Wiles and I. De Jong, Dept. of Chemistry, Carleton University, Ottawa. Personal communication.

APPENDIX 2

N.B.S. STANDARD REFERENCE MATERIAL 4957
GAMMA-RAY STANDARD
RADIUM-226

U. S. Department of Commerce
Alexander B. Trowbridge,
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate

Standard Reference Material 4957
Gamma-Ray Standard
Radium–226

This standard consists of radium-226 in approximately 5 milliliters of solution in a flame-sealed glass ampoule. The solution is 5 percent by weight HNO_3.

The weight, in micrograms, of radium-226 contained in the ampoule as of September 1, 1967, was

"$\pm 1.8_3\%$".

This standard was calibrated by comparing its gamma-ray-emission rate with those of a 1957 series of standards prepared from material that had been compared in the National Bureau of Standards radiation balance, with the national radium standards. The gamma-ray-emission rates were compared in a $4\pi\gamma$ ionization chamber containing argon at a pressure of 10 atmospheres.

The uncertainty, 1.8_3 percent, is the sum of 1.0_3 percent, which is the statistical error at the 99-percent confidence level (2.58 s_m, where s_m is the standard error), and 0.8_0 percent, which is the maximum uncertainty due to assessable systematic errors in the 1957 series of standards and in the ionization-chamber comparisons.

This standard was calibrated in the Center for Radiation Research by members of the Radioactivity Section, W. B. Mann, Chief.

Washington, D. C. 20234
March 1, 1968

W. Wayne Meinke, Chief
Office of Standard Reference Materials

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APPENDIX 3

UNCERTAINTY IN CALIBRATION FACTORS

UNCERTAINTY IN CALIBRATION FACTORS

Example 1: 18.285 Bq calibration standards for BL-5, BL-4a and DH-1a

Sample calculations for detector #1

18.285 Bq: 173965 counts/87353 sec.
background: 16 counts/75468 sec.
Ba 133 tracer: 34325 counts/44257 counts

$$\text{Calibration factor} = \left(\frac{173965}{87353} - \frac{16}{75468}\right)\frac{442573}{343256}\frac{1}{18.285}$$

$$= 0.1404 \text{ counts. Bq}^{-1}.\text{s}^{-1}$$

$$\sigma y = [\Sigma(\partial F/\partial xi)^2 \ \sigma x^2]^{1/2}$$

$$= \left[\left(\left(\frac{1}{87353}\right)\left(\frac{442573}{343256}\right)\frac{1}{18.285}\right)^2 (\sqrt{173965})^2\right.$$

$$+ \left(\left(\frac{1}{75468}\right)\left(\frac{442573}{343256}\right)\left(\frac{1}{18.285}\right)\right)^2 (\sqrt{16})^2$$

$$+ \left(\left(\frac{173965}{87353} - \frac{16}{75468}\right)\frac{1}{343256}\frac{1}{18.285}\right)^2 (\sqrt{442573})^2$$

$$\left. + \left(\left(\frac{173965}{87353} - \frac{16}{75468}\right)\frac{442573}{(343256)^2}\frac{1}{18.285}\right)^2 (\sqrt{343256})^2\right]^{1/2}$$

$$\sigma y = [1.134 \times 10^{-7} + 1.397 \times 10^{-11} + 4.455 \times 10^{-8} + 5.744 \times 10^{-8}]^{1/2}$$

$$= 0.0004641$$

The one sigma level uncertainty in the calibration factor is 0.331%

Example 2: 1.8285 Bq calibration standard for DL-1a

Sample calculations for detector #1

1.8285 Bq: 18716 counts/82760 sec.
background: 4 counts/56430 sec.
Ba 133 tracer: 38291 counts/44480 counts

$$\text{Calibration factor} = \left(\frac{18716}{82760} - \frac{4}{56430}\right)\frac{44480}{38291}\frac{1}{1.8285}$$

$$= 0.1436 \text{ counts Bq}^{-1}\text{s}^{-1}$$

$$\sigma y = [\Sigma(\partial F/\partial xi)^2 \ \sigma x^2]^{1/2}$$

$$= \left[\left(\frac{1}{82760}\left(\frac{44480}{38291}\right)\frac{1}{1.8285}\right)^2 (\sqrt{18716})^2\right.$$

$$+ \left(\frac{1}{56430}\left(\frac{44480}{38291}\right)\frac{1}{1.8285}\right)^2 (\sqrt{4})^2$$

$$+ \left(\left(\frac{18716}{82760} - \frac{4}{56430}\right)\frac{1}{38291}\frac{1}{1.8285}\right)^2 (\sqrt{44480})^2$$

$$\left.+ \left(\left(\frac{18716}{82760} - \frac{4}{56430}\right)\frac{44480}{(38291)^2}\frac{1}{1.8285}\right)^2 (\sqrt{38291})^2\right]^{1/2}$$

$$\sigma y = [1.103 \times 10^{-6} + 5.070 \times 10^{-10} + 4.638 \times 10^{-7} + 5.387 \times 10^{-7}]^{1/2}$$

$$= 0.001451$$

The one sigma level uncertainty in the calibration factor is 1.011%

APPENDIX 4

COUNTING PRECISION CALCULATION

COUNTING PRECISION CALCULATION

Example: DH-1a Subsample 3

Sample: 290160 counts/80021 sec.
Background: 16 counts/75468 sec.
Ba-133 tracer: 317582 counts/439891 counts
Calibration factor: 0.1404 counts. $Bq.^{-1}s^{-1} \pm 0.00464$1

$$\text{Activity } (Bq.g^{-1}) = \left(\frac{290160}{80021} - \frac{16}{75458}\right) \frac{1}{0.1404} \left(\frac{439891}{317582}\right) \frac{1}{1}$$

$$= 35.77\ Bq.g^{-1}$$

σy = [net count uncertainty + background factor + calibration factor + tracer factor]$^{1/2}$

$\sigma y = [4.414 \times 10^{-3} + 2.735 \times 10^{-7} + 1.398 \times 10^{-2} + 6.958 \times 10^{-3}]^{1/2}$

$= [0.02535]^{1/2}$

$= \underline{0.1592}$

Thus, <u>one sigma uncertainty</u> in DH-1a(3) is (0.1592/35.77)100% = <u>0.45%</u>